U.S. DEPARTMENT OF COMMERCE
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PB-254 919

CHEMICAL TECHNOLOGY AND ECONOMICS IN ENVIRONMENTAL PERSPECTIVES

TASK II. REMOVAL OF BORON FROM WASTEWATER

MIDWEST RESEARCH INSTITUTE

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

JUNE 1976

96031

PB 254 919

EPA-560/1-76-007

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APRIL 1976

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF TOXIC SUBSTANCES
WASHINGTON, D.C. 20460

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SPRINGFIELD VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE	5. REPORT DATE
Chemical Technology and Economics in Environmental Perspectives; Task II - Removal of Boron From Waste-Water	June 1976
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Thomas W. Lapp and Gary R. Cooper	Task II
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Midwest Research Institute 425 Volker Boulevard Kansas City, Missouri 64110	11. CONTRACT/GRANT NO.
	Contract No. 68-01-3201
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Protection Agency Office of Toxic Substances Washington, D.C. 20460	Final, February - March, 1976
	14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The purposes of this study were to determine the degree of general concern regarding the presence of boron in industrial waste streams and municipal sewage systems and to ascertain if any industries or cities are currently engaged in the removal of boron from their wastewater. For those methods currently practiced, the specific method of removal, effectiveness, and cost estimates were determined. The current literature was surveyed for other methods of boron removal that may have merit for future application in this area. Efficiency of boron removal and cost estimates were presented for several of the possible methods. A survey of the literature was also conducted to determine the effect of boron on microorganisms present in municipal waste treatment systems.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Borates Borax Boric acids Boron oxides Industrial waste treatment Sewage		Chemistry Inorganic Chemistry

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release Unlimited	Unclassified	35
	20. SECURITY CLASS (This page)	22. PRICE
	Unclassified	4.00

EPA Form 2220-1 (9-73)

CHEMICAL TECHNOLOGY AND ECONOMICS IN ENVIRONMENTAL PERSPECTIVES

Task II - Removal of Boron From Wastewater

Contract No. 68-01-3201

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Prepared for

Environmental Protection Agency
Office of Toxic Substances
Washington, D.C. 20460

June 1976

NOTICE

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PREFACE

This report presents the results of Task II of a project entitled "Chemical Technology and Economics in Environmental Perspectives," performed by Midwest Research Institute (MRI) under Contract No. 68-01-3201 for the Office of Toxic Substances of the U.S. Environmental Protection Agency. Dr. Irving Gruntfest was project officer for EPA.

Task II "Removal of Boron from Wastewater," was conducted by Dr. Thomas W. Lapp, Associate Chemist, who served as project leader, and Mr. Gary R. Cooper. This report was prepared under the supervision of Dr. E. W. Lawless, Head, Technology Assessment Section. Dr. I. C. Smith, Senior Advisor for Environmental Science, provided technical consultation. This program had MRI Project No. 4101-C.

MRI would like to express its sincere appreciation to the several companies who provided technical information for this report.

Approved for:

MIDWEST RESEARCH INSTITUTE

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Physical Sciences Division

June 28, 1976

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SECTION I

INTRODUCTION

Boron is an ubiquitous element in the natural environment. It occurs as the oxygenated forms of borate salts or boric acid and these substances are widely used for the industrial and domestic purposes. The concern for the influence of boron on life forms can be focused on three areas: (a) man; (b) plant life, both terrestrial and aquatic; and (c) lower forms of animal life, including microorganisms.

Boron has not been shown to be an essential element to man, and, while toxicity values are quoted,[1,3] some questions remain regarding its effect on man. It is essential to proper growth of plants but, at the same time, higher concentrations of boron are extremely toxic to many plant species; the differences between concentrations that are best for plant growth and toxic concentrations are often very small. For example, some citrus species require trace boron soil concentrations to produce optimum growth, yet exhibit toxic effects at the 1 ppm level in the soil. Therefore, water intended for irrigation is often classified as to its applicability to crops sensitive to boron. Most problems of toxicity to agricultural crops are confined to areas of Southwestern United States where the natural boron content of soils is appreciably higher than in other regions. In other areas where the background level is low, quantities may be added to fertilizers for positive effects on crop growth and production.[4]

Aquatic plants are also susceptible to boron toxicity. The natural boron content of surface waters averages 0.1 ppm in the United States; whereas seawater averages 4.6 ppm.[4] Boron concentrations of greater than 0.1 ppm would likely occur in discharges of industrial or domestic wastes. In the event that consumption of boron compounds in detergent formulations increases, aquatic plant life may be subjected to toxic effects from increased concentrations in the surface waters.

Another area of concern is the toxic effect of boron on microorganisms, especially those associated with sewage treatment. In trace quantities, it has been shown to be an essential element for some microorganisms.

The published literature on the effects of boron on the various sewage treatment processes is not extensive, but studies have shown that for concentrations above 10 ppm, toxic effects occur in concentrated synthetic substrate solutions.

OBJECTIVES OF THIS PROGRAM

The objectives of this program were to: (a) ascertain the degree of concern over boron in industrial waste streams and municipal sewage streams; (b) determine what industries are currently engaged in the removal of boron from their waste streams; (c) determine current methods, if any, and their effectiveness for the removal of boron as boric acid and borates from industrial waste streams and municipal waste treatment systems; (d) survey the published literature for methods of boron removal that may have merit for future application to industrial waste streams and their effectiveness; and (e) determine the effect that boron may have on the microorganisms present in the active sludge of sewage treatment processes. Wherever possible, published or estimated cost analyses for the removal of boron are to be stated for the methods found in objectives (c) and (d).

REFERENCES FOR SECTION I

1. Versar, Inc., Preliminary Investigation of Effects on the Environment of Boron, Indium, Nickel, Selenium, Tin, Vanadium, and Their Compounds, Vol. I, Boron, EPA 56/2-75-005A, U.S. Environmental Protection Agency, Washington, D.C. (1975), NTIS No. PB 245984/AS.

2. Registry of Toxic Effects of Chemical Substances, 1975 Edition, U.S. Department of Health, Education and Welfare, Public Health Service, Center for Disease Control, National Institute of Occupational Safety and Health, Rockville, Maryland, p. 231.

3. Christensen, H. E., T. T. Luginbyhl, Eds., Suspected Carcinogens, U.S. Department of Health, Education, and Welfare, U.S. Government Printing Office, Washington, D.C. (1975).

4. Sprague, R. W., The Ecological Significance of Boron, The Ward Ritchie Press, Los Angeles, California (1972).

SECTION II

SUMMARY AND CONCLUSIONS

Boron is a very common element in nature, occurring as the borate or as boric acid. While the toxicity of borate and boric acid has not been clearly established for man, it can be toxic to plants and microorganisms. The toxicity to plants requires further comment: boron is also an essential element to plant growth and the range between its beneficial and toxic concentrations can be very small. Because of increasing consumption of soaps and cleaners, the primary commercial source of boron entering the environment, an increase in the boron content of many wastewaters, and therefore many surface waters, could occur.

The purpose of this brief study was to determine the degree of general concern regarding the presence of boron in industrial waste streams and municipal sewage systems and to ascertain if any industries or cities are currently engaged in the removal of boron from their waste streams. If removal is currently practiced, the methods of removal, their effectiveness, and cost analysis were to be determined. Methods of boron removal that may have merit for future applications were also to be studied. An attempt was also made to determine the effect of boron on microorganisms present in municipal waste treatment systems.

The results of this study have shown that basically no industries or municipal sewage treatment facilities are currently removing boron from waste streams and that no real concern is presently being expressed regarding the presence of boron in either industrial waste streams or municipal sewage systems. In certain industries, boron is removed but not because of concern for the environment. California has imposed an effluent standard of 0.5 ppm for boron.

The toxic effects of boron on microorganisms found in waste streams and municipal sewage treatment facilities can vary depending on conditions. A significant reduction in microorganism activity occurred in concentrated substrate solutions at boron concentration levels greater than 10 ppm. The concentrated substrate solutions would be representative of

those present in municipal waste treatment systems. In contrast, in dilute substrate solutions approximating a waste stream, boron concentrations as high as 100 ppm showed little effect on microorganism activity.

Three methods for the removal of boron from water have been or are currently being used by industry. These methods are: (a) ion-exchange resins (Amberlite® XE-243), lime precipitation, and liquid-liquid extraction. Eight additional methods have been identified that may have varying degrees of merit for future applications in the removal of boron from waste streams.

SECTION III

BACKGROUND

This section will present a brief review of boron with respect to natural occurrence, major producers and their processes, consumption in various use areas, and losses to the environment.

OCCURRENCE[1]

Boron is a widely occurring element comprising about 0.0003% of the earth's crust, including fresh water and seawater. This compares to the most abundant metal, aluminum, which comprises 8.13%. The boron content of soils is quite variable and highly dependent upon soil porosity, amount of rainfall, specific type of soil and the quantity of soil organic matter. Igneous rocks contain the least amount of boron, averaging about 10 ppm. Sedimentary rocks contain the highest quantity, depending upon their origin, and average about 30 ppm with the highest concentration occurring in marine shales (up to 300 ppm).

A large percentage of the earth's boron is contained in the ocean, where the average concentration is about 4.6 ppm. The boron content of surface waters is generally low, e.g., 0.1 ppm average in the U.S., with a range of 0.02 ppm for the Western Great Lakes Basin to 0.3 ppm for the Western Gulf Basin.

Based on 1967 worldwide production values, coal contains an average of 75 ppm boron and the combustion of coal was estimated to contribute approximately 11,600 tons of boron, in the form of fly ash, to the world's atmosphere.[2] Data presented in another report give two values for the quantity of boron emitted to the atmosphere from coal combustion in the U.S. For 1972, values of 4,400 and 4,675 tons were given; no reasons were provided for the discrepancy in the two figures.[3]

PRODUCTION

The United States is the world's major source of boron compounds, contributing about 70% of the world production. U.S. Borax and Chemical Corporation is the leader in world production of borax and other borate chemicals.

Table 1 lists current domestic producers, locations and annual capacities.

Table 1. CURRENT BORAX PRODUCERS, LOCATIONS AND CAPACITIES[3,4/]

Company	Location	Annual capacity (thousands of tons)
Kerr-McGee Corporation		
Kerr-McGee Chemical Corporation subsidiary	Trona, California	100
	West End, California	26
U.S. Borax and Chemical Corporation	Boron, California	500
Stauffer Chemical Corporation	Trona, California	28-33

In addition to the producers of borax and refined borates listed above, Tenneco Oil Company (a division of Tenneco, Inc.) produces calcined colemanite ($Ca_2B_6O_{11}$) at Furnace Creek, California. The design capacity is approximately 77,000 tons annually.[3/]

A plant for borax production, with a design capacity of 27,000 tons, has been planned by Searles Lake Chemical Company, a subsidiary of Occidental Petroleum Corporation. The plant was scheduled for completion in 1974; however, it may have been postponed indefinitely.[3/]

CONSUMPTION OF BORON AND COMPOUNDS

Listed in Table 2 are estimated amounts and percentages of boron compounds consumed in 1973.

Miscellaneous uses included: fluxing materials, nonferrous deoxidizer, grain refiner in aluminum, thermal neutron absorbers, delayed action fuses, ignitor in radio tubes, coating material for solar batteries, abrasives, catalyst chemicals, conditioning agents for chemicals, precursor to chemicals, plasticizers, adhesive additives, fire retardants, antifreeze, textile and paper additives, biocides, photographic chemicals and as composite material.[3/]

Table 2. CONSUMPTION OF BORON COMPOUNDS IN 1973

Industry	% (as Boron)[5]	Estimated amount (tons as boron)
Glass manufacture	40-45	41,000-46,000
Soaps, cleaners	15	15,000
Enamels, frits, glazes	10	10,000
Fertilizer	5	5,000
Herbicides	2-3	2,000-3,000
Miscellaneous	25	26,000
Total		99,000-105,000

In addition, more than half of the domestic production is exported, largely as crude borates.[5] Much of this exportation goes to Europe where sodium perborate is used in detergent formulations as a bleaching agent. This contrasts with U.S. practices of using chlorine compounds in detergent formulations for their bleaching properties.

BORON LOSS TO THE ENVIRONMENT

Boron may be lost to the environment at several points during the mining and processing of the ore and during consumption of the various boron compounds by industrial and domestic users. Combustion of coal and sewage sludges are sources of loss to the environment and contribute a major portion of the boron air emissions.

Table 3 shows the estimated amounts lost to the environment in 1972; estimated losses are given for air emissions, water and solid waste discharges, and total estimated losses. The values for water and solid waste discharges were obtained by the difference between the total losses and losses through air emissions.

The major source of boron loss to water is from soaps and cleaners. Nearly all of the boron, as borax, compounded into soap, detergent and cleaner formulations is for the consumer market and does not often appear in industrial waste effluent streams. Agricultural sources of boron in water result from the use of its compounds as herbicides and also as a trace element addition to fertilizers. Railroads use large amounts of chlorate herbicides that contain a high percentage of borate as a fire retardant. Boron in industrial waste streams would arise during the processing of borax and other compounds and in the miscellaneous use categories. Some boron should also appear in water effluents from glass and ceramic manufacture.

Table 3. ESTIMATED TONS OF BORON ENTERING THE ENVIRONMENT IN 1972[3]

Category	Total amounts (air, water, solid waste)	Air emissions	Estimated water and solid waste discharges
Mining and processing	3,300	2,740	560
Glass and ceramics	1,650	1,619	31
Agricultural	7,700	1,980	5,720
Soaps, cleaners	15,400	34	15,366
Miscellaneous	2,750	550	2,200
Coal combustion	4,675[a]	4,675	0
TOTAL	35,475	11,598	23,877

a/ Two values (4,400 and 4,675 tons) for coal combustion were given in Reference 3. The air emissions value was chosen to maintain continuity within the table.

REFERENCES TO SECTION III

1. Sprague, R. W., The Ecological Significance of Boron, The Ward Ritchie Press, Los Angeles, California (1972).

2. Bertine, K. K., and E. D. Goldberg, Science, 173:233 (1971).

3. Versar, Inc., Preliminary Investigation of Effects on the Environment of Boron, Indium, Nickel, Selenium, Tin, Vanadium, and Their Compounds, Vol. I, Boron, EPA-56/2-75-005A, U.S. Environmental Protection Agency, Washington, D.C. (1975), NTIS No. PB 245984/AS.

4. Chemical Information Services, 1975 Directory of Chemical Producers, United States of America, Stanford Research Institute, Menlo Park, California (1975).

5. Wang, K. P., "Boron" in: Minerals Yearbook, 1973. Vol. I. Metals, Minerals and Fuels, Bureau of Mines, U.S. Department of the Interior, U.S. Government Printing Office, Washington, D.C. (1975).

SECTION IV

METHODS OF REMOVAL OF BORON

This section describes the current industrial and sewage treatment practices for removal of boron from waste streams, the effect of boron on municipal waste treatment systems, current and past methods of removal and potential methods for removal from waste streams.

CURRENT PRACTICES

Industrial

The practice of boron removal from waste streams occurs primarily only during the mining and primary recovery of boron from ores and brines. At no other stage in the processing were data found indicating that it is removed from waste streams.

As indicated previously, about 70% of the world production of boron originates in the U.S. and this domestic production is all located in the southeastern part of California.

United States Borax and Chemical Corporation treats wastewater effluents from its mining and primary recovery operations by evaporation of the excess water on impervious evaporation pads. In this process, ore is extracted with hot water, the liquor purified by cooling, precipitation and redissolving with hot water. The final products are sodium tetraborate, borax (decahydrate), the pentahydrate, and anhydrous sodium tetraborate.[1/] Excess process water is sent to the evaporation pads which produce no effluent. Water is recycled in the process as applicable.

The Kerr-McGee Chemical Corporation recovers borax and boric acid from the brines of the Searles Lake. Searles Lake is a dry lake and all excess process water is returned to the lake. Kerr-McGee has no true effluent water. The Kerr-McGee process entails both evaporative crystallization and solvent extraction for recovery of various salts, including

borax and boric acid.[2] Stauffer Chemical Company, also at the Searles Lake location, presumably treats its aqueous effluent by returning it to the lake.

During the secondary processing of borax and the other tetraborates to produce boric acid and other compounds, no evidence was found that industry attempts to remove boron from wastewaters. It has been reported that U.S. Borax discharges wastewater from the Wilmington, California, plant directly into the ocean.[3] This plant produces boric acid and other boron compounds using the tetraborates from their mining production.

Another secondary processor, Eagle-Picher Industries at Miami, Oklahoma, does not attempt to remove boron from the waste stream from the the manufacture of boron tribromide, boron trifluoride, and other boron compounds. The waste effluent is discharged into a sanitary sewer and has a typical analysis of < 10 ppm boron.[4]

Among the boron-consuming industries, only one reference[5] was found indicating that boron was removed from wastewater. The waste stream was from painting, cleaning, and electroplating processes. The waste treatment system was primarily for the removal of cyanide ion and chromium. Effluents from the treatment system contained 0.04 ppm boron but no initial boron concentration was stated in the article. Considering the sources of the waste stream, it is likely that the boron was initially present as the borate ion and possibly the fluoborate ion. If the fluoborate ion was initially present, the alkaline treatment conditions for the cyanide ion would have readily hydrolyzed the fluoborate ion to borate and fluoride ions by the sequential loss of fluorine.

No other instances were discovered where boron is removed from industrial wastewater streams. Inquiries to U.S. Borax[6] and Kerr-McGee[2] were made, but neither had any knowledge of industries removing boron from waste streams. Rohm and Haas Company[7] had no knowledge of any industry using their Amberlite® XE-243 ion-exchange resin to remove boron from waste streams.

Boron is considered a contaminant only in industries related to very special applications.[1] Due to its extremely high thermal neutron cross-section industries directly concerned with the production of materials and chemicals for nuclear reactors must be especially cognizant of the boron content of the water supply. The boron content in materials used in the construction and chemicals used in nuclear reactors must be very low. Seawater being used for the production of magnesium oxide and magnesium chloride brines processed for magnesium metal must maintain a low boron content if the end products are intended for use in nuclear reactors. For irrigation water, a standard of 1 ppm boron has been established but this limit is normally attained through dilution with low boron content water.

Sewage Treatment

No indication was found that any sewage treatment plants attempt to specifically remove boron from sewage wastes, either municipal or industrial. California has adopted a standard of 0.5 ppm of boron for effluent discharges from industry and municipalities. This standard was adopted primarily for the benefit of irrigation water. No attempts are being made in the waste treatment plants to specifically remove boron since the content of the incoming sewage is generally at or below the effluent discharge standard. Some violations occurred but only in the 0.7 to 0.8 ppm range and these were associated with the borax producers. At the present time, the State of California does not have any concern over the boron levels in sewage.[8-10]

Boron may be inadvertantly removed in sewage treatment through adsorption on organic matter or by absorption by microorganisms. It is an essential trace element for the growth of some microorganisms.[11] Digested sewage sludge collected from several municipal sewage treatment plants in Connecticut indicated an average boron content of 211 ppm, ranging from 160 to 360 ppm.[12] However, another widely quoted source indicates that boron is not removed by conventional sewage treatment as applied in Great Britain.[13]

Tests on the effects of boron (as boric acid and sodium borate) on a synthetic substrate have shown that boron, in slug doses, lowers the rates of biological processes. This study employed concentrated substrate solutions, approximating the corditions found in waste treatment plants. At levels greater than 10 mg/liter in an aerobic biological waste treatment plant, boron was found to appreciably lower the COD removal rate.[14] The authors did not report either the corresponding BOD removal rate or the relationship between BOD and COD for the synthetic waste under investigation. It is reasonable to assume, however, the BOD removal rate would be lower than the corresponding COD removal rate by a factor of 2 or 3. The authors concluded, however, that present levels in wastewater ($\sim$ 0.5 ppm) should pose no problems unless boron is adsorbed or concentrated on the sludge.

Another study was conducted to determine the effect of boric acid on BOD removal.[15] The study involved finding the concentration of boric acid which would produce a 50% inhibition of oxygen utilization, TC_{50}. The results for boric acid were found to be > 1,000 mg/liter, indicating that boric acid has negligible effect on the BOD test over a wide range of concentrations.

The studies described above all involved slug dosing of the synthetic sewage systems with boron compounds. In a municipal sewage system, the boron will normally be present at concentrations of about 0.5 to 1.0 ppm. In this case, the microorganisms could become acclimated to the boron and less sensitive to its toxic properties.

CURRENT AND PAST METHODS OF REMOVAL

This subsection will discuss past and present methods for the removal of boron, as boric acid and borates, from wastewater streams. Again, no evidence was found indicating that boron is currently being removed from waste streams except during mining and initial recovery of natural boron. Only two applications were found where boron is removed from process streams, aside from primary recovery of boron from ore or brines. These two applications are in the recovery of magnesium from seawater and removal of boron from water used in nuclear reactors.

The three methods which have been or are currently being used on an industrial scale for the removal of boron from water are: (a) ion-exchange resins; (b) lime precipitation; and (c) liquid-liquid extraction.

Ion-Exchange Resins (Amberlite® XE-243)

Rohm and Haas Company currently produces a boron specific ion-exchange resin, Amberlite® XE-243 (Amberlite IRA-943, the commercial designation).[16] This material is a macroreticular resin based on the amination of chloromethylated styrene-divinylbenzene with N-methylglucamine. At the present time, the primary application of this resin is in the removal of boron from seawater brines during the recovery of magnesium.[7] Extensive testing was conducted on simulated irrigation-return water by Aerojet-General Corporation, and Amberlite® XE-243 was found to be the only method available to effectively remove boron to the < 1 ppm level.[17]

Listed in Table 4 are some factors relating to boron adsorption with Amberlite® XE-243.

Table 4. BORON ADSORPTION WITH AMBERLITE® XE-243

Characteristic	Reference
1. Works best on dilute solutions	19
2. Other salts do not interfere	21
3. May be subject to chemical and/or biological degradation	17
4. Low capacity, i.e., 0.36 lb B/ft^3	20
5. High operating costs	19
6. High initial cost, i.e., \$170/ft^3	7
7. May be fouled by solids	13

Following, in Table 5, is a summary of cost estimates for a one MGD plant using Amberlite® XE-243 ion-exchange resin. These estimates are from two studies: one completed by Aero-Jet General Corporation[17] and the other by Dow Chemical Company.[18] The treated water cost does not include costs for ultimate disposal of the concentrated boron wastes generated during operation.

Table 5. COST ESTIMATES FOR DEBORONATION PLANTS USING AMBERLITE® XE-243 ION-EXCHANGE RESIN

	Aero-Jet	Dow	Dow
Capacity (MGD)	1	1	1
Resin size (mesh)	-16 + 50	-16 + 50	-40 + 50
Flow rate (gpm/ft^2)	12	10	10
Resin volume (ft^3)	310	320	320
Installed capital cost ($)	83,000	200,000	200,000
Assumed labor cost ($/hr)	2.50	4.50	4.50
Assumed power cost (¢/kwh)	0.7	0.7	0.7
Initial boron concentration (ppm)	10	10	10
Final boron concentration (ppm)	< 1	< 1	< 1
Assumed resin cost ($/ft^3)	105	105	105
Treated water cost (¢/1,000 gal)	12	23	21

In the study by Dow, estimates were also made for a 10 MGD plant. The most favorable cost per 1,000 gallons of water was about 12¢ for a plant using -40 + 50 mesh resin at a bed flow rate of 20 gpm/ft^2.

The current cost for Amberlite® XE-243 resin is as follows:

Quantity (ft^3)	Cost ($/ft^3)
40-199	171.90
200-399	170.70

At a present resin cost of $170/ft^3 3 instead of the $105 assumed in Table 5, an additional expense of approximately 7¢/1,000 gal of water should be added to the cost figures assuming a resin life of 1 year. No inquiry was made as to the availability of a resin size -40 + 50 mesh. That specification may also add to the cost of the installed resin.

It has been stated that Amberlite® XE-243 is the only currently feasible method for the effective removal of boron from dilute industrial waste streams.[6]

Lime Precipitation and Filtration

It has been reported that lime precipitation and subsequent filtration is effective to a degree in the removal of boron. Boron, in the form of boric acid or borates, is coprecipitated with other calcium salts. (Calcium borate has a solubility in water equivalent to about 620 ppm of boron.)[19] In laboratory experiments on water containing 10 ppm boron, lime precipitation was found to be less than 25% effective.[17] No cost estimates were found in the literature.

Lime precipitation also is not specific to boron, produces a sludge posing further disposal problems, and the effluent water is highly alkaline. Waggot reported about 15% boron removal from a sewage treatment effluent containing < 2 ppm boron.[13]

Because of the ineffectiveness of this process as a primary method for the removal of boron from wastewater, no cost estimates have been made for this method.

The Dow Chemical Company has used excess lime to precipitate magnesium from seawater and to prevent the coprecipitation of boron. During the precipitation process, the small quantities of boron present in the wastewater (6 to 12 ppm) remained in solution.[22] This system has been phased out in favor of an ion-exchange process based on the Rohm and Haas resin discussed in the preceeding subsection.[23]

Liquid-Liquid Extraction

A likely candidate for the removal of boron from industrial waste streams is liquid-liquid extraction. For this extraction process, a water insoluble polyhydroxy compound is dissolved in a suitable solvent which is immiscible with water and of different specific gravity. Boron is extracted from the aqueous phase into the solvent phase by complexation.

Boron, as borax, is presently extracted from weak brines by Kerr-McGee Corporation in this manner. This system was developed specifically for weak brines and plant end liquors having boron concentrations of the order of 1.7%.[24] No data were presented for the low concentrations (10 ppm) anticipated in wastewater so the potential applicability of the system to waste streams is unknown. No cost data relative to the weak brines were presented in any of the publications.

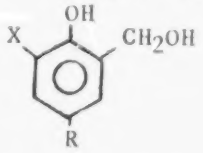
Table 6 lists several patented chemical compounds reportedly usable for liquid-liquid extraction of boron.

An article reviewing the patent U.S. 3,111,383 assigned to American Potash and Chemical Corporation indicated that more than 25 compounds were cited in the patent.[25] Table 7 lists some of the compounds and carrier agents.

Table 6. LIQUID-LIQUID EXTRACTION REAGENTS

Chemical name	Patent No.	Patent holder
1,8-Naphthalenediol	Brit. 910,541	American Potash and Chemical Corporation[a]
5-(1,1,3,3-tetramethylbutyl) salicylic acid	U.S. 3,839,222	E. A. Grannen
Polyol[27,b]		Dow Chemical Company
4-t-Butyl-catechol[22]		Dow Chemical Company
6 to 16 Carbon aliphatic diol or triol	U.S. 2,969,275	American Potash and Chemical Corporation
15 Annular carbon homocyclic aromatic polyol	U.S. 3,111,383	American Potash and Chemical Corporation
Substituted catechols[c]	U.S. 3,424,563	Dow Chemical Company
7 to 20 Carbon substituted hydroxy benzyl alcohols	U.S. 3,424,563	Dow Chemical Company
8 to 20 Carbon aliphatic vicinal diol	U.S. 3,433,604	Dow Chemical Company
3 to 12 Carbon alkyl or alkoxy substituted 4-catechol	U.S. 3,433,604	Dow Chemical Company
Halogen substituted 4-catechol	U.S. 3,433,604	Dow Chemical Company

a/ Now subsidiary of Kerr-McGee Corporation.[28]

b/ 

c/ Used in conjunction with 12 to 30 carbon water immiscible alkyl ammonium salts.

Table 7. BORON EXTRACTION COMPOUNDS AND SOLVENT CARRIERS[25]

Extraction compound	Solvent carrier
2-Chloro-4-(1,1,3,3-tetramethylbutyl)-6-methylolphenol[a]	Kerosen
1-2-Diphenylglycol	Methyl isobutyl ketone and tributylphosphate
2,6-Dimethylol-4-octylphenol	Kerosene and decanol (1:1)
2,6-Dimethylol-4-nonylphenol	Kerosene and decanol (1:1)
4,6-Dichlorosaligenin	Benzene and decanol
4-t-Butyl-6-chlorosaligenin (90%)	Benzene
4-t-Butyl-6-methylsaligenin (90%)	Kerosene
4-Chloro-6-cyclohexylsaligenin (90%)	Octanol

a/ While this compound was listed as the preferred compound in the patent, all of the other compounds had a relative extraction coefficient at least as high or higher than the preferred compound. The principal problems associated with the other compounds relate to extractant stability and solubility in water. The preferred compound has a distribution coefficient of 80 (ratio of percent boron in organic phase to aqueous phase).

Solvent extraction studies in 36% magnesium chloride brine solutions, at initial boron concentrations of 0.21 to 0.85 g/liter, confirmed the affinity of 4-t-butyl-catechol for boron in the form of boric acid.[22] However, one test showed poor extraction results at low (12 ppm) boron concentration: 10 ppm boron remained in the aqueous phase. For aqueous systems, of the type encountered in most waste streams, the solubility of t-butyl catechol in water would probably prevent this system from being highly efficient. The substitution of larger alkyl groups for the t-butyl group may decrease the water solubility and improve the efficiency. However, no studies have been conducted on the effect of different alkyl groups in the solubility. Using t-butyl catechol, it has been estimated that the cost of this system would be approximately $0.50 to 0.75/1,000 gal.[26]

POSSIBLE METHODS OF REMOVAL

In this subsection, methods having potential for the removal of boron, as boric acid and borates, from industrial waste streams will be discussed.

Strong Basic Anion-Exchange Resins

Ion-exchange resins of the strongly basic type could be used to remove boron from industrial waste streams.[7] Two major drawbacks would occur with the use of these resins: (a) strong basic ion-exchange resins are highly pH dependent, i.e., maximum absorption is at pH 7.5 to 9.0 with almost no absorption at pH 5;[13] and (b) strong basic ion-exchange resins are not specific to boron.[6]

A patent, U.S. Patent 3,856,670, was issued to Occidental Petroleum Corporation for an anionic ion-exchange resin, which reportedly will selectively remove borates from water.[29] The resin was produced by the co-condensation reaction of an aromatic orthohydroxy acid, a phenolic compound and an aldehyde. The patent claimed that borate is removed in the presence of alkali, alkaline earth, nitrogen organic bases and ammonium cations. No figures were presented with respect to efficiency or cost.

A French patent has been granted for the removal of boron from discharged process waters by fixation, in the form of boric acid, on an anionic ion-exchange resin followed by elution with alkali.[30] A test solution, originally containing 2,600 ppm boron, showed 151 ppm after one run through the resin. Recycling the effluent reduced the boron concentration to 47 ppm. No information was presented for solutions containing low concentrations of boron (~ 10 ppm) nor were any cost estimates included in the abstract.

No evidence was found to indicate that industry is currently using these resins to remove boron, nor were any operating costs found in the literature.

Adsorption on Clay Materials

It has been reported that boron may be adsorbed by certain clay materials from water[19] but three montmorillonite micas and one bentonite clay were tested with water containing 10 ppm boron and none were found to remove boron.[17]

Distillation of Boron Containing Waters

A process has been patented for removal of boron from water by distillation of a liquid waste containing 21,000 to 22,000 ppm boron.[31] The distillate still contained 50 to 80 ppm of boron. Upon passing the distillate through a 6-ft bed of ceramic Raschig contact rings, the boron content was reported to have been reduced to 2 to 3 ppm boron.[2] No cost estimates were reported for this process.

Although no indication was found of any current use in industry, the process has potential application in the decontamination of nuclear reactor coolants.

Alumina-Lime-Soda Ash[32]

The alumina-lime-soda water treatment process was developed as a unique method for softening brackish water, especially those containing major quantities of calcium and magnesium sulfate, prior to desalination in a reverse osmosis system. An important bonus of this process is its ability to remove boron and other ions from brackish water. Raw water, doped with 1.7 ppm boron, was treated by this process and the posttreatment water was found to contain 0.2 ppm boron. Both lime and sodium aluminate are required to achieve boron removal as neither constituent alone will remove this component.

Unit costs for a system designed to remove boron, and estimated on a basis similar to that used for costing ion-exchange systems, would be $0.20 to $0.25/1,000 gal. for a 1 MGD plant.[33]

Ion-Exchange Resin Produced by Condensation of Catechol and Formaldehyde

In the work done by Roberts et al.,[17] it was thought that an ion-exchange resin produced by the condensation of catechol and formaldehyde could be effective in removing boron from irrigation return waters. This was based on the fact that the formation constant for catechol-basic boric acid complexes is very large. The desired physical properties of the product

resin were not met in their experiments and the resin did not effectively remove boron from the test solution. No recent literature has appeared indicating that an ion-exchange resin of this type has received further attention.

Complexation of Boron and Rejection by Reverse Osmosis

In the work by Roberts et al., it was suggested that boron may be complexed with water soluble organic polyhydroxy compounds to form a molecular species which, due to size and ionic character, would tend to be membrane impermeable in the reverse osmosis process.[17] In these studies, the six materials tested as possible complexing agents were: mannitol, fructose, polyvinyl alcohol, tartaric acid, catechol, and a soluble starch. Only catechol proved to be reasonably effective in boron reduction. For a test solution containing 10 ppm boron, catechol showed an effectiveness of about 70%. All other materials showed an effectiveness in the range of 30 to 45% with the same test solution. Since these particular studies considered only systems with an effectiveness of ~ 90% to be acceptable, no further studies relating to cost or other factors were undertaken.

A recent study has presented cost analyses for the reverse osmosis treatment of brackish water and seawater.[34] For a 3 million gallon per day (MGD) operation using a hard water feed and a 95% water recovery, the cost was $0.77/1,000 gal. These figures are based on 1972 dollars. The membranes were of the hollow fiber (Permasep®) type. Based on the rapidly advancing technology of reverse osmosis and cost estimates for the new operation to be based at Yuma, Arizona, it was estimated that future costs for brackish water treatment would be approximately $0.36 to $0.37/1,000 gal. based on a 1,000 ppm inlet feed and a 90% rejection rate. While this study was not directed specifically towards boron removal, the projected costs should be applicable to its removal. For an initial boron concentration of the order of 10 ppm, the cost of the catechol (based on 40 ppm) to be added during the pretreatment process would result in a cost of $0.45 to $0.75/1,000 gal., depending upon the quality of the catechol. Current prices for catechol are $1.35/lb (tech grade) and $2.25/lb (CP grade).

A cellulose acetate butyrate (CAB) reverse osmosis membrane has been developed and preliminary research indicates a better rejection rate of uncomplexed boron, as boric acid,[35] than the more conventional cellulose acetate (CA) membrane. However, the flux, i.e., the amount of water permeating 1 sq ft of membrane per day, was considerably lowered.

Following is a summary of the comparative results:[35]

Membrane	Flux (gal/ft^2, membrane/day)	% Boric acid rejected
CA	26	18
CAB	8	53

The boric acid rejection of 53% is not considered an acceptable value in most studies and feed solution had an initial concentration of 1,700 ppm boric acid. Most of the studies reviewed indicate that approximately 80% or more rejection is considered acceptable. While this membrane could make the problem of complete organic complexation less critical than with the cellulose acetate membrane more generally used at the present time, no studies have been conducted at concentrations of about 10 ppm of boron to test the effectiveness of this system at those levels. No cost information was stated for the CAB process.

Distillation Separation of the Methanol-Boron Azeotrope[36]

The possibility of separation of boron, in the form of borates, by this method arises from the common analytical separation technique. In this procedure, methanol is combined with an aqueous hydrochloric acid solution containing the boron. The azeotrope, $B(OCH_3)_3$-CH_3OH, is distilled from the original solution into water.

The azeotrope can then be hydrolyzed with excess base and the methanol recycled by distillation. The boron remains in the second aqueous solution and could be disposed as a solid by evaporation of the water. Since this method is used for the quantitative determination of boron, the efficiency would be expected to be high (~ 98%).

This separation procedure would be applicable only to streams containing high boron loading, since the volume of distillate would be excessively large for the removal of small concentrations of boron. It is possible that the method would be useful for process streams or other instances of high boron concentration, but not for normal wastewater or municipal sewage streams containing low boron concentrations. No cost figures were found in the published literature.

Specially Prepared Active Carbon

A Japanese patent, Japan 74 37,035, outlined a method for preparing activated carbon capable of adsorbing boron from waste or seawater.[37] The preparation of the carbon involved the following steps:

1. Active carbon is added to a soluble salt or solution of iron.

2. The mixture is then hydrolyzed.

3. The insoluble iron hydroxides are consequently absorbed by or deposited on the active carbon.

The above prepared substance adsorbs boron and other metal ions. No costs or efficiencies were listed in the reference.

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